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PB-258 920-T

The Carcinogenic Properties of Oil Shale Products and the Possibilities of Prophylaxis of Cancer

Environmental Protection Agency, Research Triangle Park, N C

1972

BIBLIOGRAPHIC DATA SHEET	1. Report No. EPA TR76-54	3.	PB 258 920-T

4. Title and Subtitle

The carcinogenic properties of oil shale products and the possibilities of prophylaxis of cancer

5. Report Date: 1972

6.

7. Author(s): G.O. Loogna

8. Performing Organization Rept. No.

9. Performing Organization Name and Address

TRANSLATED FROM RUSSIAN BY EPA

10. Project/Task/Work Unit No.

11. Contract/Grant No.

12. Sponsoring Organization Name and Address

Translation Service
Office of Administration - Library
Research Triangle Park, NC
27711

13. Type of Report & Period Covered

14.

15. Supplementary Notes

Nauch.-prakt. deyatel. inst. eksp. klin., Tallin, 1972, pp.105-113

16. Abstracts

17. Key Words and Document Analysis. 17a. Descriptors

EPAISD

17b. Identifiers/Open-Ended Terms

ENVIRONMENTAL HEALTH

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

17c. COSATI Field/Group 06P 5TH

PRICES SUBJECT TO CHANGE

18. Availability Statement: THIS TRANSLATION WAS MADE FROM A NON-COPYRIGHTED TEXT	19. Security Class (This Report) UNCLASSIFIED	21. No. of Pages 16
	20. Security Class (This Page) UNCLASSIFIED	22. Price $3.50-3.00

300050

TR 76-54

THE CARCINOGENIC PROPERTIES OF OIL SHALE PRODUCTS AND THE POSSIBILITIES OF PROPHYLAXIS OF CANCER [Kantserogennyye svoystva slantseproduktov i vozmozhnosti profilaktiki raka]

by

G.O. Loogna

Published in Nauch.-prakt. deyatel. inst. eksp. klin., Tallin, 1972, pp. 105-113

A systematic study of the carcinogenic properties of products of thermal processing and incomplete combustion of Estonian (kukersit) oil shales was made at the Institute of Experimental and Clinical Medicine MZ ESSR [Ministerstvo zdravookhraveniya, Ministry of Public Health, Estonskaya Sovetskaya Sotsialisicheskaya Respublika, Estonian Soviet Socialist Republic] beginning at the time of its founding in 1947 upon the initiative and under the directorship of Professor P.A. Bogovskiy. The basic data of experimental morphological research done by him are presented in two monographs [1, 2]. In these studies, coworkers of the Institute participated and continue to participate, A.I. Vysamyae, Kh. K. Turu, I.A. Veldrye, F. Yu. Vinkmann, Kh. Yu. Mirme. Moreover, work has been done in this field at the Tartusk State University

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Translated for NERC-Library, EPA, from the Russian by LEO KANNER ASSOCIATES, P.O. Box 5187, Redwood City, California 94063, (415) 365-3046, August 1975.

and at certain other scientific institutions of the Soviet Union. For example, the carcinogenic effect of products of Weimar and Gdov shales related in origin and composition to the Estonian shales, were studied by L.F. Larionov, N.G. Soboleva, and L.M. Shabad even in 1934. Data exist on the blastomogenic activity of chamber and generator tars and tars of tunnel furnaces for Estonian shales (L.F. Larionov, 1947; O.L. Danetskaya, 1952; L.P. Nurmand and co-authors, 1955; G.M. Gortalum, 1955). However, this information was incomplete and partially contradictory. Therefore, coworkers of our Institute took on the problem of obtaining more complete and detailed data on the carcinogenic properties of the basic primary oil shale products, commercial products, and also shale soot. A considerable amount of material was accumulated for the elapsed period and was published in various publications. A short survey of these studies is presented below.

In total, the experimental work was done on 4500 animals mainly white mice; rats and rabbits were also used in some of the work. The test methods included applying the substance being studied on the hair-covered skin of the mice in the interscapular region; the soot suspensions were introduced intratracheally. Pieces of skin, internal organs and swollen lymphatic nodes were taken for histological study. The results of the tests were treated statistically. The physical and chemical and toxological characteristics of the basic products of shale-chemical industry are presented in an article by E. Ya. Blinova and Kh. Ya. Yanes in this collection.

Four basic primary products of thermal treatment of shale were studied: generator, chamber and tunnel tar of the shale processing

combine, "Kokhtla-Yarvye" im. V.I. Lenin and tar from equipment with a solid heat-carrying agent at the "Kiviyl." combine.

P.A. Bogovsky [2] studied the carcenogenic effect of generator tar obtained by distilling shale at 450--500° C; a content of 3 4-benzpyrene (BP) of 0.01% was established in the sample. It appeared that in relation to the number of mice living up to the appearance of the first tumor, 28.8% developed benign tumors and only in singular cases were there signs of the beginnings of cancer. In tests with chamber tar obtained at 900--1000° C and with a content of 0.1% BP 55.7% of the mice who survived to the appearance of the first tumor were discovered to have neoplasms and 55.1% of these were malignant. In Kh. T. Vakhter's [4] similar tests on rabbits, in all cases, benign fibroepithelial tumors of the skin developed. When applying solid fractions of generator tar, malignancy was observed in 8.5% and with the effect of chamber tar--in 21.7%. Consequently, the chamber tar obtained at higher temperature contains 10 times more BP and has a stronger carcinogenic activity in comparison with generator tar.

Kh. K. Turu [18] pointed out that tar of equipment with a solid heat-carrying agent obtained at a temperature of 500--530° C shows an average carcinogenic effect less clearly expressed than in chamber tar. The sample of tar studied also has considerably less sharp general toxic and local damaging effect on the skin than does chamber tar.

Tunnel tar obtained at a temperature of distillation 400--500° C contains only 0.001% BP and has average carcinogenic activity. In relation to the number of mice surviving to the first tumor, the total quantity of mice affected by tumors amounted to 35.0% and the number of

mice with malignant tumors—was 6%.

The data presented above on the carcinogenic properties of average-temperature tars obtained mainly in tests on miscellaneous breeds of mice are controversial. Therefore, F. Yu. Vinkmann [6] made a comparative study of the degree of carcinogenicity of these tars. In tests lasting up to 18 months it was established that the average of the fractions of average-temperature tars have moderate carcinogenic activity. They cause both benign and malignant tumors of the skin in mice of the CC57 BR line; generator tar causes tumors in 48.5%, tar from equipment with a solid heat-carrying agent—in 36% and tar of the tunnel furnace—in 35% of the animals. According to P.A. Bogovskiy's data, generator tar is blastomogenic to a high degree causing only benign tumors in a significant part of the white mice. From F. Yu Vinkmann tests it is noted that the generator tar is both blastomogenic and has a moderate carcinogenic effect. More than half of the tumors were malignant. In various data of the authors mentioned, to some degree, higher toxicity of samples of generator tar is apparent in the tests of P.A. Bogovskiy in which all the animals died during a 9 month period. In this time period, malignant tumors obviously could not successfully develop.

Thus, carcinogenic activity of the products being studied is higher, the higher the temperature of processing the shale and the specific weight of the tar. The contents of BP in the resins obtained at higher temperatures also is higher and this can give one an idea of the carcinogenic effect of tar in biological tests.

Considering the carcinogenicity of oil shale products, when planning industrial equipment, it is necessary to plan for maximum hermetic seal

and automation of production processes in order to completely avoid contact of workers with carcinogenic products.

In the products of thermal treatment of fossil fuels it is necessary to determine not only the BP but also other carcinogenic substances. It is known, for example, that BP is very carcinogenic for mice but does not cause tumors in dogs, monkeys and certain other animals. There is no direct proof that BP itself is the most powerful carcinogen for man. There is evidence on the development of industrial related tumors which occur due to the effect of substances which do not contain BP. In the tars of Estonian oil shale not only BP is observed. In one sample of tar from equipment with solid heat-carrying agents, O.G. Eyzen and P. Kh. Arro [18] from the Institute of Chemistry of the AN ESSR [Akademiya nauk, ESSR, Academy of Sciences of the ESSR] the presence of 1,2-benzpyrene, 1,2-benzantracene, and 2-methyl-1,2-benztracene were determined.

By repeated chromographic processing of the chamber tar, 9 fractions were separated which differed in content of BP [19]. P.A. Bogovskiy [2] established that fractions exist in which the BP is not observed but which have a blastomogenic effect. One of these fractions caused benign and malignant tumors of the skin in mice, but tumors did not occur when the substance was introduced into the muscle. However, with both methods of introduction, tumors developed in the lungs. Another fraction not containing BP caused papillomata of rabbits but did not lead to the development of neoplasm in the skin of mice; at the same time tumors in the lungs occurred. The fraction being discussed increased the carcinogenic effect of other fractions which contain only a certain amount of BP. In the fractions which contain the main part of the BP,

there exist, apparently, other substances which considerably lengthen the latent period of the tumors, but do not decrease the frequency of their appearance and their malignancy in comparison with the effect of the synthetic BP in the same concentration.

P.A. Bogovskiy [2] also studied various commercial products of the shale oil industry (anthacene oil, furnace fuel oil, oil plasticizer, drying oil, bitumen), which contained in their composition one or another quantity of chamber tar. The author convincingly pointed out that the addition of chamber tar increased the carcinogenic activity of these commercial products. Since then, a method of coking the chamber tar has been introduced [3], to prevent its addition to the commercial product.

F. Yu. Vinkmann [7] studied the blastomogenic activity of DFK-4 resin glue, a shale solvent and a shale pyrolytic varnish--LSP-1. This varnish is manufactured on a base of solvent and resin of pyrolysis of shale gasoline. This can be used as a substitute for bitumen varnishes and for manufacturing paints. In tests of mice of the CC57BR line it was shown that LSP-1 varnish not only has 100% blastomogenic effect on the skin of the mice but also is clearly carcinogenic, inasmuch as more than half of the tumors were malignant. Shale solvent and DFK-4 resin glue did not show a blastomogenic effect. Inasmuch as the varnish consists of solid residue of pyrolysis products of shale gasoline and dissolving solvent, the latter does not have a blastomogenic effect and the blastomogenic and carcinogenic properties of the varnish are mainly included in the first component. Consequently, for purposes of prophylaxis of cancer in humans when working with the residues of pyrolysis products of shale gasoline it is necessary to completely exclude

the possibility of dust, solutions and aerosols of this products falling on the skin and mucous membranes.

One should also forbid the use of residues of pyrolysis products of shale gasoline as the bases for varnishes, and also for other purposes without preliminary decarcinogizing of the product.

Shale products and waste waters of chemical combines contain various phenols. Considering the contradictory data on the role of phenols and carcinogenesis, a comparison was made on chamber tar and phenol-free chamber tar. The latter contains 0.2% BP and has a more clearly expressed carcinogenic effect than does the whole chamber tar. This difference can depend both on the concentration of active components of the tar and on the elimination of the continuing effect on carcinogenesis of the shale phenols [2].

Kh. Yu. Mirme [14] studied both the so-called total water soluble phenols of shale waste waters, and also their crystal fractions "A" and "B." Considering the peculiarities of the potency or co-carcinogenic effect of phenols, a sub-carcinogenic dose of BP (0.36 mg) was premiminarily applied to the skin of mice (CC57BR) and during a 10 day period--50% acetone solutions of phenols. The total phenols were the most carcinogenic. Skin tumors occurred in 48.6% of the mice (of these 88% were malignant). The weakest carcinogenic effect was in the "B" fraction--tumors developed in 23% of the mice (of these 50% were malignant). Under the effect of "A" fractions, tumors occurred only in 8.6% of the animals. Considering the total effect on the influence of BP and phenol fractions one can conclude that the "A" fractions have a very weak effect.

From this data it follows that water soluble shale phenols have a strong carcinogenic effect. The co-carconogenic effect of a 50% solution of total phenols can be equalized in the effect of a 10% solution of phenol (hydroxybenzene) is one of the strongest.

It is interesting to note that the use of methods of chemical kinetics permits giving a quantitative evaluation of the relationship of catalyst-carcinogenic properties of phenols on their structure and to predict the character of effect and camparative activity of a homolog of given structure before setting up biological tests. With the Hammet-Taft equation it was established, for example, that phenol which has a clearly expressed catalyst-carcinogenic capacity, has weak toxicity, and the reverse [12]. Further accumulation of experimental data permits giving a quantitative description of the relationship of anti-tumor properties of phenols to their structure and to establish the principles and connections with other phenomena of activity of these compounds.

The content of shale phenols in waste water should be looked at both from a general hygienic viewpoint and from an oncological point of view. In the waste waters of the "Kokhtla-Yarvye" combine BP was observed in a quantity of 0.02 to 9 mg/l [10]. Then, in the total discharge before dephenolization, the content of BP amounted to 0.2 mg/l, and after dephenolization--0.005 mg/l. Consequently, the process of dephenolizing decreases the concentration of BP in the waste water by approximately 40 times, apparently, as a result of its separation by butyl acetate. According to the data of I.A. Veldrye and co-authors [5], waste waters of the "Kiviyli" combine contain before dephenolization 0.005 mg/l BP. After dephenolization by a method of evaporation, the

concentration of carcinogen decreased only to 0.002 mg/ℓ (2.5 times) which gives us evidence of the great effectiveness of the method of extraction with butyl acetate. In view of the fact that during extraction of the main mass, the BP remains in the extract of dry phenols used as a component part in the production of the tanning agent, during operation with the extracts one should use all prophylactic measures planned for operation with carcinogenic products.

According to statistical data, the illness rate of cancer of the breathing organs in the Estonian SSR, in comparison with other republics, is considerably higher. Epidemiological researchers, M.K. Purdye, E.K. Khint, V.A. Taygro [16] from our Institute pointed out that the illness rate of cancer of the lungs is considerably greater in the oil shale oasin where the air constantly contains products of incomplete combustion of fuel shales.

The circumstances indicated were an incentive to A.I. Vysamyae [9] to clarify in tests on animals what kind of a role the soot of shale solid and liquid fuel plays in the etiopathogenesis of cancer of the lungs. In order to do this white rats were injected 10 times intratracheally with tar substances extracted from the soot of the oil shales, suspended in two different media: in a 12.5% aqueous solution of Tween 40 and in peach oil. The results of the tests supported the possibility of developing tumors of the lungs under the effect of tar substances from soot of fuel shales which contain 0.0107% BP.

In another work by A.I. Vysamyae [8] it was established that tumors of the skin in the location of applying gasoline extract of soot of solid shale fuel (with an additive of liquefied vaseline) occurred in

78% of mice. Beginning with the fifth month of the test, papillomata developed, the majority (62%) of which developed into malignant tumors. The carcinogenic character of the soot is explained by its content of 0.0014% BP (in the gasoline extract 0.04 mg per 1 ml). The blastomogenic effect of the gasoline extract of soot of shale mazut (liquid fuel) is considerably weaker than with soot of shale solid fuel.

The facts presented point out the necessity for serious preventive measures for combatting shale oil smoke.

The possibilities of prophylaxis of cancer. When studying the blastomogenic properties of shale products date were obtained on the morphogenesis of induced tumors and certain general principles of chemical carcinogenesis of the skin and lungs are clarified. However, the main importance of the results obtained include the fact that they permit validating the necessity for a number of prophylactic measures. Some of these were mentioned above. The technical, hygienic and medical means of prophylaxis of cancer are described in more detail in the monographs of P.A. Bogovskiy [1, 2]. General positions on the complex preventive combat of malignant tumors in conditions of our republic are considered in an article by G.O. Loogna [13]. From these works and the data presented above it follows that impermissible carcinogens in production and in life require the earliest and most radical measures for prophylaxis of cancer. One of these measures is developing those production procedures in which the carcinogenic substances will not form or will break down to a significant degree, that is, will be decarcinogenized.

P.A. Bogovskiy with co-authors [3] developed an industrial method of decarcinogenizing, the essence of which consists of treatment of the

tar resin before coking. The initial tar contained 0.19--0.23% BP, its solid fraction--0.64%. The distillate obtained during coking of heavy fractions contained only 0.05--0.06% BP, that is, it was 10 times smaller. A 15% gasoline solution of the initial tar caused tumors of the skin in 68% of the mice who survived to the appearance of the first tumor. Then, 44% of the mice had malignant skin tumors. The distillate caused keratosic papillomata in the location of application only in one mouse out of 50 (3.7%) and in another mastocytoma of the skin; not one malignant tumor was noted. Thus, a tar treated according to the method posed practically completely avoids blastomogenic properties. The content of BP in the coke is 2.5 times lower than in the initial tar and approximately the same as in the distillate.

The author was given an author's certificate for the invention and the n.. method was put into practice. Beginning in 1965, in a the city of Kokhtla-Yarvye a mill for coking has been operating and putting out industrial products. The proposed method we have mainly used also for decarcinogenization of products of thermal treatment of other fossil fuels. Thus, coking of carcinogenic tars is a process which has a definite value for the prevention of cancer.

M. Ya. Gubergrits, P.A. Bogovskiy and others [11] studied the possibility of decreasing the carcinogenic activity of shale tars (0.1% by weight BP) with high voltage electrical charge. In series I (50 kV 0.0044 μV, 250 impulses) the concentration of BP in the tar was decreased to 0.0023%. In the second series of tests (30 kV, 0.6 μV, 50 impulses), accompanied by plasma probing of the liquid, the content of BP decreased to 0.003%. Skin lubricated with the treated tar in 300 days caused

tumors in 51.8% (series I) and 53.3% (series II) of surviving animals, and the use of the initial tar—in 97.9%. Moreover, in the test groups the tumors were less malignant and their quantity fewer than in the control groups. The physical and chemical characteristics of chamber tar treated with an electrical charge was practically unchanged.

Other new fields have opened up for decarcinization of shale oil products. For example, it was shown [16] that under the effect of ultra violet radiation, BP in an aerated medium is changed

which results in eliminating the carcinogenic properties. A similar effect is also obtained when using ionizing radiation, ozone, chlorine and so forth. However, the change in content of 1 BP or other carcinogenic hydrocarbons does not yet give us information on the initial decrease of blastomogenic activity of one or another product. All the results of the biological studies are decisive at the present time.

The information presented in this article tells us that the malignancy of organs must continuously be fought in order to make it possible to establish the maximum permissible concentrations of carcinogens (DPK [predel'no dopustimyye kontsentratsiya, maximum permissible concentrations]). Considering the experience of Soviet hygienists in combatting toxic harmful substances one can propose that the introduction of strict DPK of carcinogenic agents will also direct technical thought in the search for reliable ways of eliminating carcinogenic substances from the media surrounding man.

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